

Direct Simulation of Ultrafast Detonations in Mixtures

Patrick D. O'Connor^{*}, Lyle N. Long^{*} and James B. Anderson[†]

^{*}*Department of Aerospace Engineering, The Pennsylvania State University, University Park, PA 16802, USA*

[†]*Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA*

Abstract. For nearly a century experimental measurements of the velocities of detonations in gases have been found in general agreement with those of the Chapman-Jouguet (C-J) hypothesis predicting velocities, relative to the burned gases, equal to the speed of sound in the burned gases. This was further supported by the Zeldovich - von Neumann - Döring (ZND) theories predicting Chapman-Jouguet velocities for detonations in which the shock and reaction zones are separated. However, for a very fast reaction, the shock and reaction regions overlap and the assumptions required for the C-J and ZND theories are no longer valid. Previous work with the direct simulation method established conditions for forcing the reaction and shock regions to coalesce in a detonation wave by means of a very fast exothermic reaction. The resulting detonation velocities were characterized as ultrafast, as they were found to exceed the steady-state velocities predicted by the C-J and ZND theories. Continued investigation into the ultrafast regime has allowed for the further development of this inconsistency with theory by including a heavy non-reacting gas in the mixture. The resulting gaseous mixtures closely followed the C-J predicted behavior for slow reactions, and for very fast reactions were found to produce ultrafast detonations with a substantially greater deviation from C-J behavior.

INTRODUCTION

The possibility of ultrafast detonations - those exceeding the Chapman-Jouguet detonation velocity - was predicted about a year ago and demonstrated in DSMC calculations for model systems [1]. It is not known whether such ultrafast detonations can be produced with conventional chemical reactions, such as $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$, in laboratory experiments or with nuclear reactions, such as those occurring in supernovae [2]. If conventional reactions are not sufficiently fast to produce ultrafast detonations it might be possible to produce them by decreasing the speed of sound as by adding a heavy inert gas to the reactant mixture. In this paper we report DSMC calculations of detonations for several such mixtures. We find for fast reactions that the increase in detonation velocity relative to the C-J velocity is proportionately greater for ultrafast detonations in mixtures with added heavy gases. This increases the likelihood that ultrafast detonations can be observed experimentally.

SIMULATION DETAILS

Using the DSMC method originally developed by Bird in 1963 [3,4], numerical simulations of detonations involving multiple species reactive flow were completed. The time-accurate, three-dimensional code was written in C++ with an object-oriented approach using ensemble averaging of results from each run. The code was written with the option of either periodic or specular boundaries and would initiate the reaction by quickly increasing the temperature in a small number of cells near the left or right-most boundary. Note that the current results consider only monatomic particles and one dimension of propagation. The numerical simulations treated the particles as hard spheres with no internal energy. Typical cases ran for approximately 12 to 24 hours on a 2.8 GHz Pentium processor and required between 250 and 500 MB of RAM.

The DSMC code was written in object-oriented C++. Through inheritance, polymorphism and encapsulation it was possible to write a code that is significantly easier to read, maintain, modularize, etc. than the typical top-down design of many C or FORTRAN codes. The DSMC code is broken down into two primary classes, a *particle* class and a *cell* class. The *particle* class governs the properties and movements of each individual particle such as its

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 13 JUL 2005		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Direct Simulation of Ultrafast Detonations in Mixtures				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Aerospace Engineering, The Pennsylvania State University, University Park, PA 16802, USA				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM001792, International Symposium on Rarefied Gas Dynamics (24th) Held in Monopoli (Bari), Italy on 10-16 July 2004. , The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

mass, velocity, position, diameter, as well as methods to find which cell a particle is in and the thermal ignition of the system to initiate reactions. The *cell* class contains the methods for collisions, reactions, the cell sampling techniques, and flow property computations (velocity, temperature, number density, etc. of each species). The *cell* class contains an array of particles as data members.

REACTION AND DETONATION CHARACTERISTICS

A detonation wave travels at supersonic velocity in a reactive gas mixture and is driven by energy released from the exothermic reactions within the wave. Work by Chapman in 1899 [5] and Jouguet in 1905 [6] laid the foundation for the theoretical treatment of detonations. The properties of a detonation wave were derived from the conservation equations and the Chapman-Jouguet condition which assumes the detonation wave, relative to the burned gases, is equal to the speed of sound in the burned gases. In the 1940's, Zeldovich [7], von Neumann [8], and Döring [9] independently justified the C-J condition based on stability arguments, but were only able to do so assuming that the shock wave precedes the reaction, i.e., that the regions are separated. They were unable to make similar justifications for the case where the shock and reaction regions overlapped and left this aspect of the problem unresolved. In this work we have investigated the overlapping event in terms of four individual cases which consider both fast and slow reactions in both a single species gas and more complex mixtures. The present work follows naturally our previous work in simulating chemical reactions [10-13], detonations [1, 14, 15], nonlinear acoustics [16, 17], and blast waves [18] using DSMC.

Single Reactive Species (Cases I & II)

Case I and Case II refer to single species unburned gases with normal and ultrafast detonations, respectively. Consider first the simplest irreversible bimolecular reaction $A + M \rightarrow B + M$ (where $M = A$ or B), and the masses and diameters of A and B are equal. The particles are treated as monatomic hard spheres with no internal energy. The amount of energy released on reaction, Q , is fixed per molecule reacting and the minimum activation energy, E^* , varies according to the desired rate of reaction. Cases I and II are considered single reactive species problems because the gas initially contains only the unburned, or reactant, gas (species A). Note that for collisions of A with A , only one A was allowed to react and the energy released by any reaction was added to the energy of the colliding partners and distributed in terms of the post-collision velocities. Cases I and II considered slow and fast reactions respectively, and applied the initial upstream conditions and activation energies shown in Table 1. The results for these cases reproduce previous calculations by Anderson and Long [1] predicting ultrafast detonations.

Reactive Gas Mixtures (Cases III & IV)

For Cases III and IV the unburned gas is a mixture of light and heavy particles. Case III simulates a slow reaction producing a normal detonation wave while Case IV refers to a fast reaction resulting in an ultrafast detonation. These two cases represent more complex systems due to the presence of the non-reacting heavy particles in the unburned gas. The overall reaction is the same as Cases I and II with the additional representative reaction $C + M \rightarrow (NR)$, or no reaction. The rationale for including the heavy inert species is apparent when one considers the Chapman-Jouguet velocity, D_{CJ} , of the detonation wave relative to the unburned gases given by

$$D_{CJ} = \frac{n_2}{n_1} \sqrt{\frac{\gamma k T_2}{m_2}} \quad (1)$$

where γ is the specific heat ratio, n is the number density, k is the Boltzmann constant, and T_2 and m_2 are the temperature and mean molecular mass of the burned gases, respectively. When considering the variables in Equation 1 it is now obvious how the addition of a heavy inert particle to the gas system will decrease the Chapman-Jouguet detonation velocity. The inert C particles added to form the equilibrium mixtures were loosely modeled after Xenon, and as a result were 6.5 times more massive than the reacting A particles. In addition, when computing the C-J temperature and velocity only the fraction of reacting molecules per mole were used when accounting for the amount of energy released on reaction since only a specified concentration of the overall mixture would be designated as reactants.

TABLE 1. Conditions for Simulations

Particle Type:	Hard sphere
Exothermicity:	8 kcal/mol
Minimum Activation Energy:	1 kcal/mol (fast reaction) 10 kcal/mol (slow reaction)
Molecular Weight:	20 kg/kmol (A and B) 130 kg/kmol (C)
Diameter:	4.41×10^{-10} meters (A, B and C)
Particles per cell:	500
Ratio of real to simulated particles:	1.0
Upstream mean-free-path:	4.9×10^{-6} meters
Upstream temperature:	10 K
Number of cells:	3000
Cell length:	1/40 MFP
Time-step size:	$\sim 10^{-11}$
Mean collision time:	$\sim 10^{-8}$

RESULTS

As previously described, four cases will be presented simulating both slow and fast reactions. Cases I and II have only product and reactant species while Cases III and IV have product, reactant and non-reacting species. Numerous cases with varying concentrations of the non-reacting gas were completed, but only the cases of 0% (Cases I and II) and 25% (Cases III and IV) concentration of species C will be presented in detail here. In addition, Figure 5 displays the temperatures of each individual species for Cases III and IV and Figure 6 displays the detonation velocities for varying concentrations of the non-reacting particle C. The activation energies considered were $E^* = 10$ (for Cases I and III) and $E^* = 1$ (for Cases II and IV) which produced detonations driven by slow and very fast reactions, respectively.

Single Reactive Species (Cases I & II)

The results obtained from the DSMC simulations with a single reactive species exhibited a close correlation to theory for slow reactions producing normal detonation waves. For the case of $E^* = 10$ kcal/mol, a normal detonation wave was obtained and the velocity closely matched the C-J predicted value. Figure 1 shows the temperature and species concentration through the detonation wave. For Case I there is a distinct separation between the temperature rise (i.e. the shock wave) and the species concentration rise (i.e. the reaction). The midpoint of the shockwave is near the start of the reaction zone. While the two effects are not completely separated, they do tend to support the assumption used by von Neumann, et al. in order to validate the C-J condition.

After establishing the strong correlation between the DSMC results and the C-J and ZND theories, the case of overlapping shock and reaction regions was investigated. As previously stated, the C-J and ZND theories are not necessarily valid for cases with overlapping regions. The details of the detonation wave for Case II, which had very fast reactions, are shown in Figure 2. For this reaction the shock and reaction zones are almost completely merged together. This case produced a detonation velocity exceeding that of the C-J velocity and is designated here as an ultrafast detonation. The most significant divergence from theory was approximately 6%.

Reactive Gas Mixtures (Cases III & IV)

As interpreted from Equation 1, the addition of the heavy non-reacting gas to the initial distribution of particles effectively lowers the C-J velocity since it is calculated using the mean molecular mass of the burned gas. Figures 3 and 4 show temperature and species number density through the detonation wave for Cases III and IV.

Case III was a slow reaction mixture that produced a normal detonation wave traveling at a velocity nearly identical to the C-J velocity. This case was simulated using a 25% concentration of C particles and with $E^* = 10$

kcal/mol. Note again that the shock zone and the reaction zone overlap somewhat but are separated. The typical von Neumann spike is also observed as it is a characteristic of normal detonation waves. Case IV considered the very fast reaction in the unburned mixture and is shown in Figure 4. The reaction and shock zones are almost completely overlapping and the overall number density change is very small through the detonation wave. This very fast reaction case produced a detonation wave with a velocity 46% faster than that of the C-J velocity.

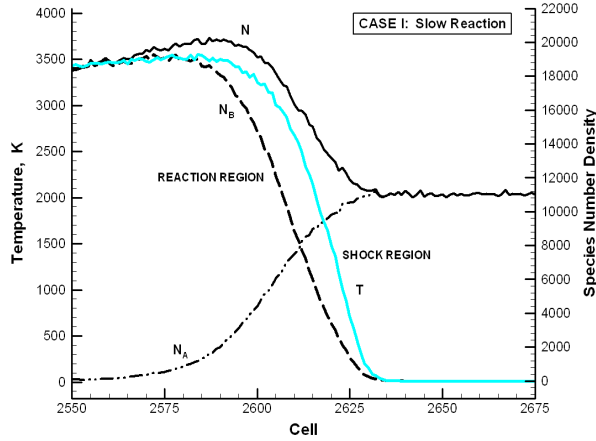


FIGURE 1. Profile for normal detonation. *Case I.*

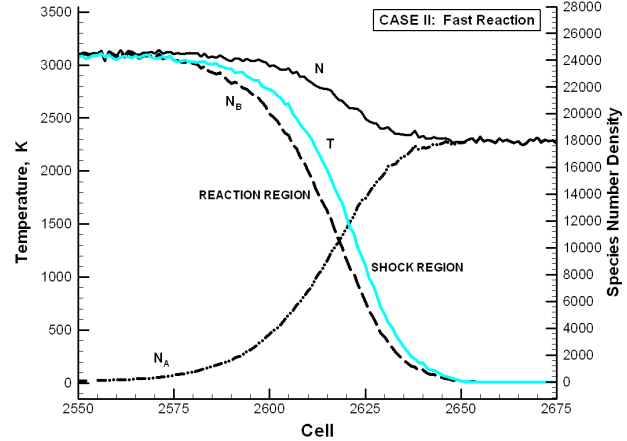


FIGURE 2. Profile for ultrafast detonation. *Case II.*

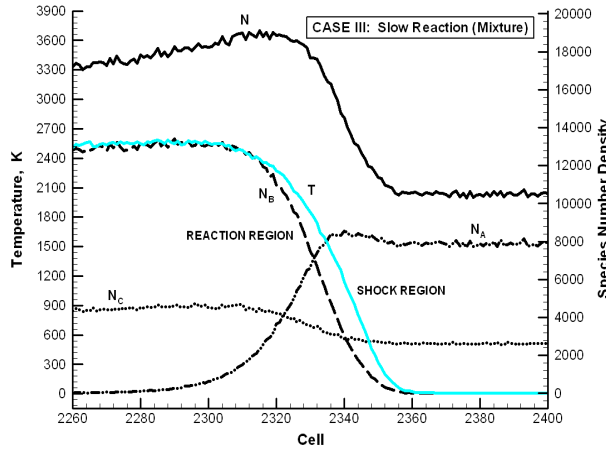


FIGURE 3. Profile for normal detonation. *Case III.*

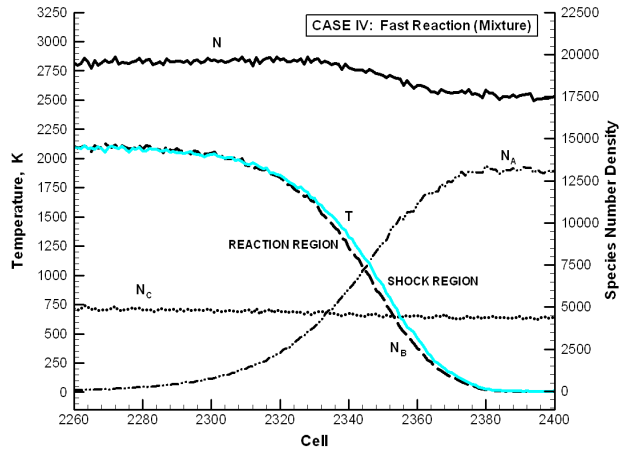


FIGURE 4. Profile for ultrafast detonation. *Case IV.*

It is also possible to measure the individual species temperatures for the product, reactant, and non-reacting particles. This was based on the single species thermal velocity measured relative to the average velocity of that particular species, and not that of the mass average velocity. This is represented simply as $\mathbf{c}_p'' = \mathbf{c}_p - \overline{\mathbf{c}_p}$, where p is the species of interest. Substituting this in place of the thermal velocity (which is measured relative to all species) \mathbf{c}_p' , into the general form for species translational temperature gives

$$T_{tr_p} = \frac{3}{2} m_p \overline{\mathbf{c}_p''^2} / k \quad (2)$$

Figure 5 shows the species temperature profiles for Cases III and IV. Note that as the number of particles of each species approaches zero there is increased statistical scatter in the species temperature, as expected. They also

show a very small number of the particles formed after the reaction (B) are ahead of the detonation, and are at a high temperature relative to the translational temperature.

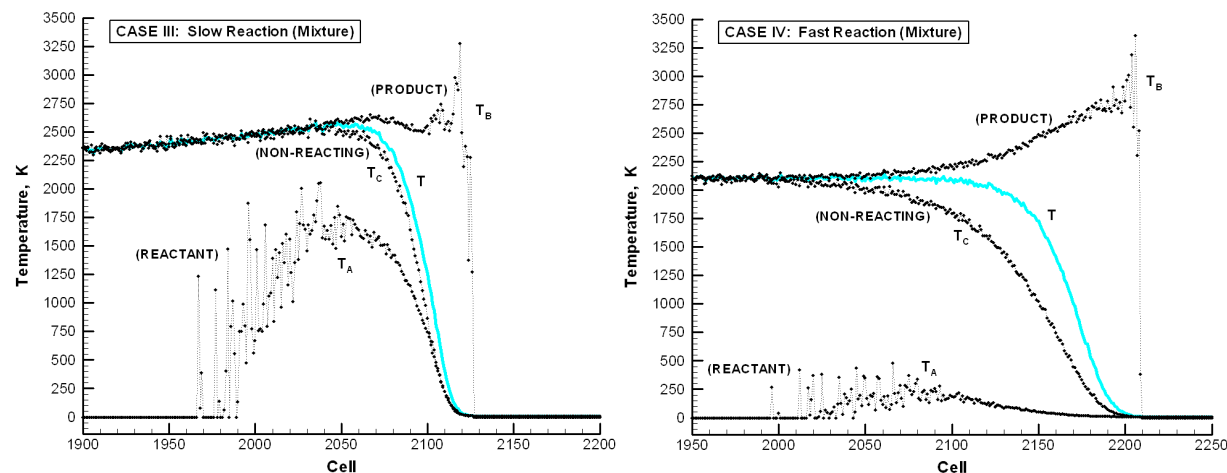


FIGURE 5. Individual species temperature profiles for slow and fast reactions in mixtures.

Figure 6 shows the detonation velocity for a range of activation energies for several different concentrations of species C. The increase in concentration of species C causes the detonation velocity to decrease. Also, the ultrafast detonation velocity effect seems to be enhanced by the addition of heavy particles. Table 2 lists the maximum detonation velocity calculated for varying concentrations of C and its velocity relative to the C-J value. Note that for a concentration of 50% C particles the detonation velocity is approximately 58% higher than the C-J velocity. For slow reactions all cases give very nearly the C-J velocity.

TABLE 2. DSMC Velocities

For $E^* = 1$ kcal/mol		
$c[C]$	D (m/s)	D/D_{CJ}
0%	2578.32	106%
5%	2422.57	115%
10%	2286.52	123%
20%	2089.52	139%
25%	2002.80	146%
30%	1845.06	147%
40%	1649.11	156%
50%	1409.01	158%
60%	1141.79	153%
75%	648.68	120%

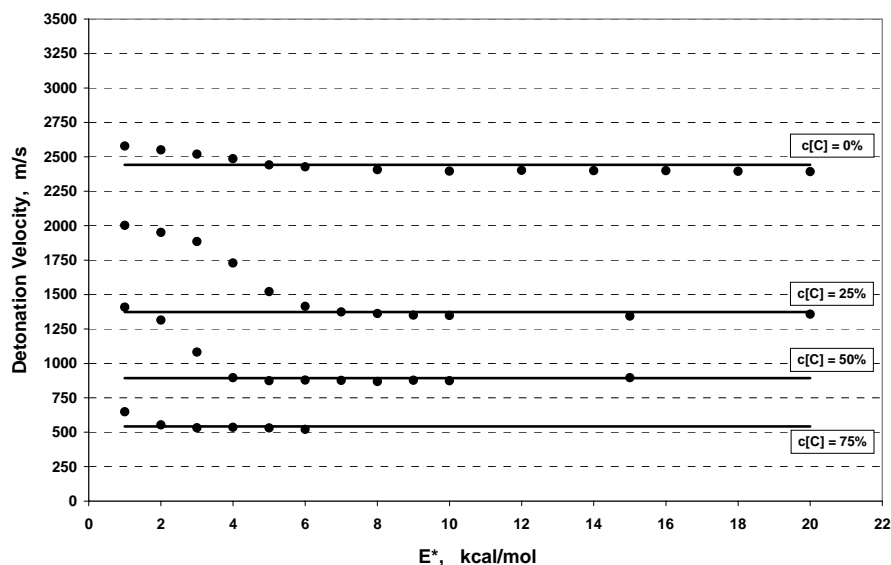


FIGURE 6. Detonation velocities for varying concentrations of non-reacting C particles.

CONCLUSIONS

The purpose of this research was to investigate ultrafast detonations for varied gas mixtures and predict the effect of added heavy gases. The validity of the Chapman-Jouguet velocity associated with the overlapping of shock and reaction regions could not be substantiated in the early 1940s, leaving a break in our understanding of how such a case would behave. This research has been one of the few significant studies to consider this problem, and it is one of the few modern cases of simulations preceding experiment. Based on these results, we expect to see these predictions verified experimentally as one should be able to observe ultrafast detonations in the laboratory more readily with the addition of a heavy non-reacting gas.

ACKNOWLEDGMENTS

We would like to thank the National Science Foundation for funding the Consortium for Education in Many Body Applications, CEMBA (<http://www.cemba.psu.edu>), grant no. NSF-DGE-9987589.

REFERENCES

1. J. B. Anderson and L. N. Long, *J. Chem. Phys.* 118, 3102-3110 (2003).
2. G. J. Sharpe, *Mon. Not. R. Astron. Soc.* 322, 614-624 (2001).
3. G. A. Bird, *Phys. Fluids* 6, 1518-1519 (1963).
4. G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Clarendon, Oxford, 1994).
5. D. L. Chapman, *Phil. Mag. (London)* 47, 90 (1899).
6. E. Jouguet, *J. Mathématique* 347 (1905); 6 (1906).
7. Y. B. Zeldovich, *J. Exptl. Theoret. Phys. (U.S.S.R.)* 10, 542 (1940); translated in *NACA Tech. Memo.* 1261 (1950).
8. J. von Neumann, *O.S.R.D. Rept. No. 549* (1942); *Ballistic Research Lab. File No. X-122*.
9. W. Döring, *Ann. Physik.* 43, 421 (1943).
10. S. D. Piersall and J. B. Anderson, *J. Chem. Phys.* 95, 971 (1991).
11. S. D. Piersall and J. B. Anderson, *Chem. Phys. Lett.* 189, 95 (1992).
12. S. M. Dunn and J. B. Anderson, *J. Chem. Phys.* 102, 2812 (1995).
13. S. M. Dunn and J. B. Anderson, *J. Chem. Phys.* 99, 6607 (1993).
14. L. N. Long and J. B. Anderson, in *Rarefied Gas Dynamics, 22nd International Symposium* (T. J. Bartel and M. A. Gallis, Eds.), *Am. Inst. Phys.*, pp. 653-657 (2001).
15. J. B. Anderson and L. N. Long, in *Rarefied Gas Dynamics, 23rd International Symposium* (A. D. Ketsdever and E. P. Muntz, Eds.) *Am. Inst. Phys.*, pp. 186-193 (2003).
16. A. L. Danforth and L. N. Long, to appear *J. Acoustical Society of America*, 2004.
17. A. L. Danforth and L. N. Long, 24th *Rarefied Gas Dynamics Conference*, Bari, Italy, 2004.
18. A. Sharma and L. N. Long, to appear *J. Comp. Physics*, 2004.